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Tin-oxide-coated single-walled carbon nanotube bundles supporting platinum electrocatalysts for direct ethanol fuel cells

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Abstract

Novel tin-oxide (SnO₂)-coated single-walled carbon nanotube (SWNT) bundles supporting platinum (Pt) electrocatalysts for ethanol oxidation were developed for direct ethanol fuel cells. SnO₂-coated SWNT (SnO₂-SWNT) bundles were synthesized by a simple chemical-solution route. SnO₂-SWNT bundles supporting Pt (Pt/SnO₂-SWNTs) electrocatalysts and SWNT-supported Pt (Pt/SWNT) electrocatalysts were prepared by an ethylene glycol reduction method. The catalysts were physically characterized using TGA, XRD and TEM and electrochemically evaluated through cyclic voltammetry experiments. The Pt/SnO₂-SWNTs showed greatly enhanced electrocatalytic activity for ethanol oxidation in acid medium, compared to the Pt/SWNT. The optimal SnO₂ loading of Pt/SnO₂-SWNT catalysts with respect to specific catalytic activity for ethanol oxidation was also investigated.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

A direct ethanol fuel cell (DEFC) is a promising technology for power supply for transportation and portable electronic device applications. Ethanol is energy-dense (1325.31 kJ mol⁻¹), readily available from biomass resources and has a distinct advantage over methanol because it is non-toxic [1–4]. Furthermore, at room temperature, ethanol is in the liquid state and, unlike hydrogen, can be easily stored and transported using the current gasoline infrastructure with only slight modifications [5, 6]. Despite these advantages, DEFCs have been hindered in becoming viable as a marketable commercial product primarily due to (i) slow reaction kinetics at the anode, (ii) low catalyst tolerance to reaction intermediates and (iii) poor performance due to unfavorable end-product selectivity [7–9].

The discovery of a tolerant and highly active ethanol oxidation fuel cell catalyst is the ultimate goal for many researchers. This task has proven to be extremely complicated as ethanol electrocatalysts face the difficult task

of cleaving a C–C bond, which is necessary to oxidize ethanol to its complete combustion products to yield a 12-electron pathway [10]. Commercial carbon-black-supported platinum (Pt/C) catalysts are unable to realize the 12-electron pathway and instead produce acetic acid (four-electron pathway) and acetaldehyde (two-electron pathway) as major products which yield much lower overall performance [11]. Unmodified Pt/C catalysts are also prone to poisoning in a DEFC due to reaction intermediates, such as CO, that may bind to platinum (Pt) reactive sites [12]. Many studies have shown that the addition of metal oxides (SnO₂, RuO_x, RhO_x, MnO_x) to carbon-supported Pt yields greater oxidative removal of CO species and results in a more tolerant and durable electrocatalyst [13–17]. Of these studies, tin oxide has shown tremendous promise for ethanol oxidation in its ability to promote the oxidation of reaction intermediates and increase catalytic activity through the well-known bifunctional mechanism with Pt reaction sites [18–21]. Various studies also report the successful creation of a Pt-based electrocatalysts supported by multi-walled carbon nanotubes (Pt/CNT) [2, 22–24]. The physical properties of CNTs can be dramatically influenced by surface

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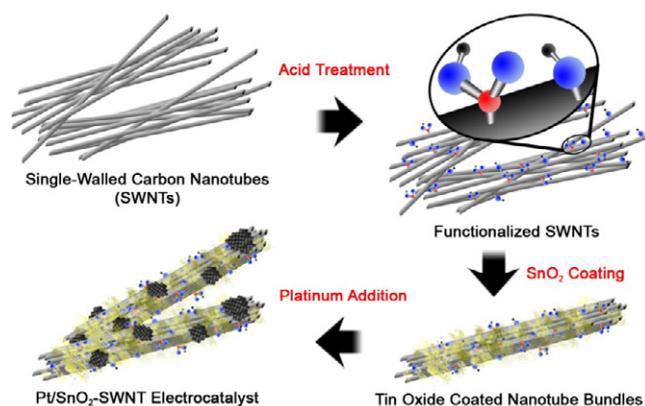


Figure 1. Schematic of synthesis procedure for Pt/SnO₂-SWNTs.

modification with selected organic, inorganic and biological species. Such functionalization can lead to a significant enhancement of catalytic properties. It has been reported that Pt/SnO₂-CNT/graphite outperformed Pt/SnO₂/graphite electrodes, having higher electrocatalytic activity, better conductivity and long-term stability [2, 24]. Single-walled carbon nanotubes (SWNTs) have been more frequently investigated as advanced electrocatalyst supports due to their unique structural, mechanical and electrical properties [23, 25].

In this study, we proposed an effective process to prepare tin-oxide (SnO₂)-coated single-walled carbon nanotube bundles supporting Pt (Pt/SnO₂-SWNT) electrocatalysts. The prepared catalysts are active towards ethanol electro-oxidation at room temperature. The synthesis procedure of the Pt/SnO₂-SWNT catalysts is illustrated in the schematic of figure 1. SWNTs were first acid treated to functionalize the surfaces before coating the outer layer with SnO₂. These bundles of SnO₂-SWNT composites were then decorated with platinum using a polyol reduction process. The electrocatalytic activity for ethanol oxidation of the resulting Pt/SnO₂-SWNTs was compared with that of Pt/SWNTs. Furthermore, the loading of the SnO₂ on the catalyst support was varied to optimize the Pt/SnO₂-SWNT electrocatalysts using different precursor ratios of SnCl₂·2H₂O to SWNT.

2. Experimental section

2.1. Synthesis of SnO₂-SWNTs

To synthesize the SnO₂-SWNT supports, a known amount of tin precursor (SnCl₂·2H₂O) was dissolved into 200 ml of DDI water and mixed with 7 ml of 38 wt% HCl. 100 mg of SWNTs was dissolved into a separate beaker containing 200 ml of DDI water and stirred until good dispersion was achieved. The tin precursor solution was added to the SWNTs and the resulting mixture was ultrasonicated for 30 min. The mass ratio of SnCl₂·2H₂O to SWNT for each of the composite supports was 10:1, 50:1 and 250:1, denoted in this report as SnO₂-SWNT-1, SnO₂-SWNT-2 and SnO₂-SWNT-3, respectively. After sonicating, the mixture was filtered, washed with DDI water and then dried overnight at 70 °C.

2.2. Deposition of Pt onto SnO₂-SWNTs

The addition of Pt onto SnO₂-SWNT or SWNT supports was carried out by a well-known polyol process, where ethylene glycol was used as a reducing agent. 160 mg of support material was sonicated in 80 ml of ethylene glycol until acceptable dispersion was achieved. 106.2 mg of platinum precursor (H₂PtCl₆·6H₂O) was dissolved in 8.0 ml of ethylene glycol. This resulting chloroplatinic acid mixture was added to the support mixture in a drop-wise fashion and mixed for an hour at room temperature.

The mixture was made basic (pH > 13) by adding 2.5 M NaOH in ethylene glycol before it was heated to 130 °C for 3 h. The system was refluxed with a water condenser tube and argon was made to flow over the surface while stirring. The mixture was then allowed to cool to room temperature and the pH was lowered to 4 using a 1 M solution of HCl in H₂O. The solution was filtered to recover the catalyst materials, which were subsequently washed with warm deionized water to remove residual solvents. The remaining catalyst materials were dried at 70 °C overnight.

2.3. Physical characterization

All samples were analyzed by x-ray diffraction (XRD), transmission electron microscopy (TEM) and thermogravimetric analysis (TGA). Monochromatic Cu Kα x-rays (0.154 nm) were used with an Inel XRG 3000 diffractometer to conduct the XRD analysis. A broad range scan of 2θ from 0.288° to 113° was carried out for about 10 min on each sample. TEM was conducted using a Philips CM 300 at 300 kV. A SDT 2960 Simultaneous DTA device was used to thermally decompose approximately. Samples were all heated from 40 to 900 °C at a rate of 20 °C min⁻¹.

2.4. Electrochemical characterization

A PINE instrument AFCBP1 biopotentiostat was used to conduct the cyclic voltammetry electrode experiments which were employed for the electrochemical characterization of all the electrocatalyst samples. The CV conditions were as follows: 0.1 M HClO₄ electrolyte saturated with N₂ gas, scan rate of 50 mV s⁻¹ and Pt loading of 40 μg cm⁻² at room temperature. Similar conditions were used to evaluate the ethanol oxidation reaction (EOR) of all samples where an electrolyte of 0.1 M HClO₄ with 1.0 M CH₃CH₂OH was made and used in place of the perchloric acid.

3. Results and discussion

Thermogravimetric analysis was carried out to determine the resulting SnO₂ loading on the SnO₂-SWNT composites. Figure 2 illustrates the thermograms for each sample. A clear trend can be seen between the amount of precursor salt utilized in the composite and the thermal stability. Thermal degradation begins at around 500 °C, 550 °C and 575 °C for the SnO₂-SWNT-1, SnO₂-SWNT-2 and SnO₂-SWNT-3 composite samples, respectively. Pure SWNTs were analyzed using TGA and displayed typical weight loss caused by

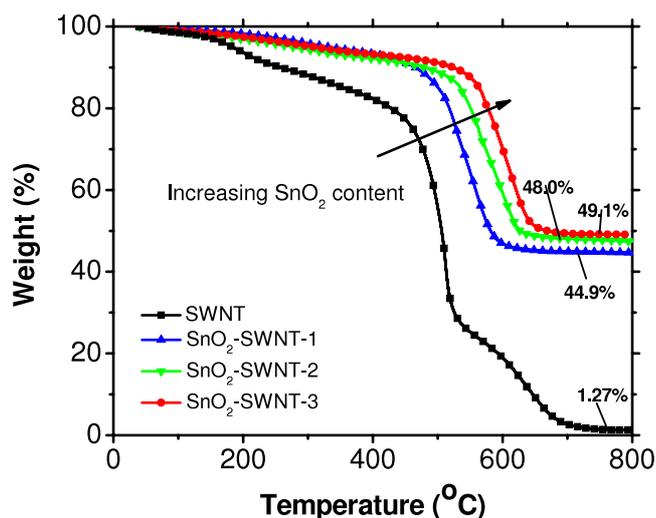


Figure 2. TGA thermograms of SWNT, SnO₂-SWNT-1, SnO₂-SWNT-2 and SnO₂-SWNT-3.

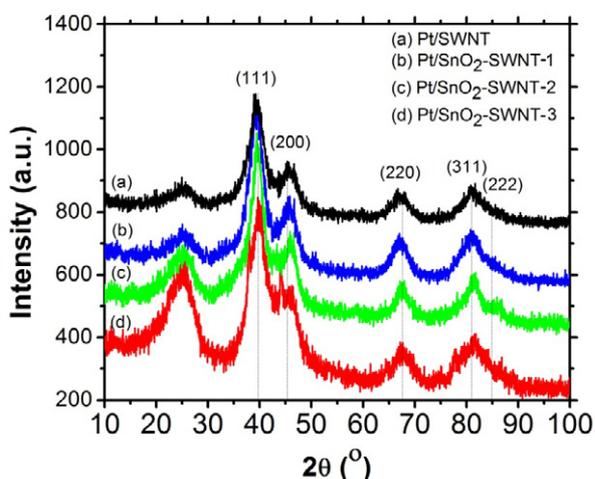


Figure 3. XRD patterns of (a) Pt/SWNT, (b) Pt/SnO₂-SWNT-1, (c) Pt/SnO₂-SWNT-2 and (d) Pt/SnO₂-SWNT-3.

moisture removal at temperatures less than 350 °C followed by a rapid weight loss starting at approx. 400 °C. By 700 °C, the final weights of all the samples were assumed to have all the carbonaceous species burned off, leaving behind any impurities in the SWNTs and the dry mass of SnO₂.

The SnO₂ loading of each composite was determined by reading the final mass percentage remaining at 800 °C and subtracting the final mass remaining by the SWNTs. It was realized that there was a diminishing return on the final SnO₂ remaining on the SWNTs. A fivefold increase in the amount of precursor salt added to the SWNTs did not yield a fivefold increase of SnO₂ on the composite. From the TGA thermograms, the SnO₂ mass loading of the composites approached a maximum of about 50%. Excess SnO₂ could be washed away during filtration of the SnO₂-SWNT composites. Platinum nanoparticles were then deposited onto SWNT, SnO₂-SWNT-1, SnO₂-SWNT-2 and SnO₂-SWNT-3 to create the four different catalyst materials denoted as Pt/SWNT,

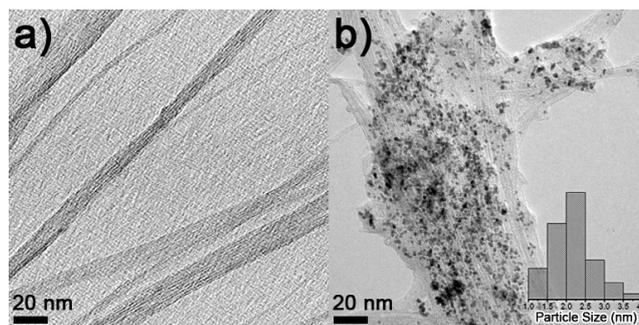


Figure 4. TEM images of (a) SWNT and (b) Pt/SnO₂-SWNT-2. Inset shows the Pt particle size distribution.

Pt/SnO₂-SWNT-1, Pt/SnO₂-SWNT-2 and Pt/SnO₂-SWNT-3, respectively.

The mean platinum particle size for the different catalyst materials can be estimated from Scherrer's equation:

$$d = \frac{K\lambda}{B \cos \theta} \quad (1)$$

where d is the particle diameter (nm), K is the shape factor (0.89), λ is the wavelength of the x-rays (0.154 nm), B is the full width at half-maximum of the peak (rad) and θ is the Bragg angle (°) [26, 27]. Figure 3 shows the diffraction patterns of the different catalysts with the platinum peaks at approx. 39°, 46°, 67°, 81° and 86° corresponding to the (111), (200), (220), (311) and (222) faces of platinum, respectively [4, 28]. All particle size calculations were estimated based on the Pt(220) peak which yielded platinum particle sizes of 2.1, 2.4, 2.4 and 2.3 nm for Pt/SWNT, Pt/SnO₂-SWNT-1, Pt/SnO₂-SWNT-2 and Pt/SnO₂-SWNT-3, respectively.

All platinum catalysts showed similar particle diameter sizes attained by the ethylene glycol reduction method. This method has been reported to accurately control the particle sizes of various metal additions to carbon supports. Thus it is reasonable that platinum deposited onto all the supports yielded particle sizes in the small range of 2.1–2.4 nm.

A peak at approx. 26° is observed within all samples in figure 3. This peak is a result of the (002) graphitic face of carbon and the (110) face of SnO₂ [29]. This peak is seen in the Pt/SWNT sample where it is entirely the result of the (002) graphitic carbon face: however, the intensity of the peak gradually increases as the SnCl₂·2H₂O precursor ratio is increased; another good indication that the SnO₂ loading was varied for each of the samples.

High resolution TEM images of unmodified SWNT and Pt/SnO₂-SWNT-2 are shown in figures 4(a) and (b), respectively. At a glance, the platinum particles added onto the SnO₂-SWNT-2 support show good dispersion and uniform platinum sizes. The inset in figure 4(b) represents the particle size distribution of one hundred platinum particles. Through TEM, the average particle size of platinum on the Pt/SnO₂-SWNT was calculated to be 2.2 nm which is in good accordance with XRD data. A comparison of the images also reveals that the Pt/SnO₂-SWNTs aggregate to form bundles which are much thicker than the SWNT in figure 4(a). This

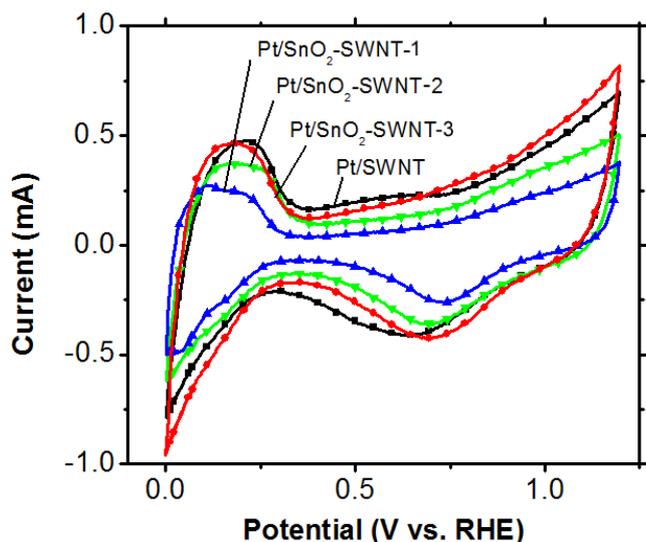


Figure 5. Cyclic voltammograms of Pt/SWNT, Pt/SnO₂-SWNT-1, Pt/SnO₂-SWNT-2 and Pt/SnO₂-SWNT-3 in 0.1 M HClO₄.

may be attributed to the SnO₂ which was found to coat arrays of SWNTs evenly on the outer carbon surface.

Voltammetry was employed to electrochemically characterize each catalyst sample (figure 5). Cyclic voltammograms were conducted in acidic media and utilized to calculate the electrochemical active surface area (ECSA) by the following equation:

$$\text{ECSA} = \frac{Q_H}{m \times c} \quad (2)$$

The charge for hydrogen desorption, Q_H (mC cm⁻²), was determined by integrating the hydrogen desorption region and dividing by the potential scan rate. The values of 0.4 and 0.21 were used for the mass loading, m (mg cm⁻²), and the charge to oxidize one monolayer of hydrogen on Pt, c (mC cm⁻²), respectively [30]. ECSA values of 55.3, 65.1, 68.6 and 77.3 m² g⁻¹ were calculated for Pt/SWNT, Pt/SnO₂-SWNT-1, Pt/SnO₂-SWNT-2 and Pt/SnO₂-SWNT-3, respectively. Such a result is counterintuitive with XRD data. Pt particle sizes from XRD were shown to be smallest in the Pt/SWNT catalysts, yet

ECSAs were much larger for the other samples. This result demonstrates that the SnO₂ has a positive effect on the ECSA of the catalytic material. The general trend indicates that higher SnO₂ loadings in the composite yield greater ECSAs. This result is in line with results obtained by Jiang *et al* which attributes this effect to the bifunctional mechanism, which involves hydroxyl removal at Pt sites by the SnO₂ species on the catalyst [31]. Due to this effect, a higher platinum utilization can be realized using Pt/SnO₂ composites to allow for low platinum catalysts.

Cyclic voltammograms were also conducted in ethanol oxidation conditions to examine the suitability of the catalyst material for DEFCs. Pt/SWNT showed the lowest current density of the four different catalytic samples, indicating that the addition of SnO₂ had a positive effect on the catalytic activity of the Pt/SnO₂-SWNT catalysts. Figure 6(a) illustrates the voltammograms of the catalysts working in EOR conditions with the peak current densities (mA cm⁻² electrode) at 1.25 V versus RHE labeled in the graph. These peak current densities were 39, 23, 21 and 14 mA cm⁻² for Pt/SnO₂-SWNT-2, Pt/SnO₂-SWNT-1, Pt/SnO₂-SWNT-3 and Pt/SWNT, respectively. It is worthwhile noting that the highest loading of SnO₂ did not yield the best EOR activity. These results were then normalized by plotting surface specific activity (mA cm⁻² of Pt) over the potential scan range (figure 6(b)) which yielded similar results. Therefore, for the samples assessed, a 50 to 1 ratio of SnCl₂·2H₂O precursor salt to SWNT ratio yielded optimum results for the EOR.

4. Conclusions

Pt/SnO₂-SWNT electrocatalysts were developed for direct ethanol fuel cells. This novel catalyst was successfully synthesized and optimized by varying the SnO₂ loading in the SnO₂-SWNT bundles supporting the electrocatalyst. A mass ratio of 50:1 of precursor salt (SnCl₂·2H₂O) to SWNTs led to an electrocatalyst with the highest current density at 1.25 V versus RHE for the EOR. It was determined that this ratio allowed for optimization of the bifunctional mechanism to increase surface specific activity without oversaturation of SnO₂ to cause a decline in electron conductivity of the material.

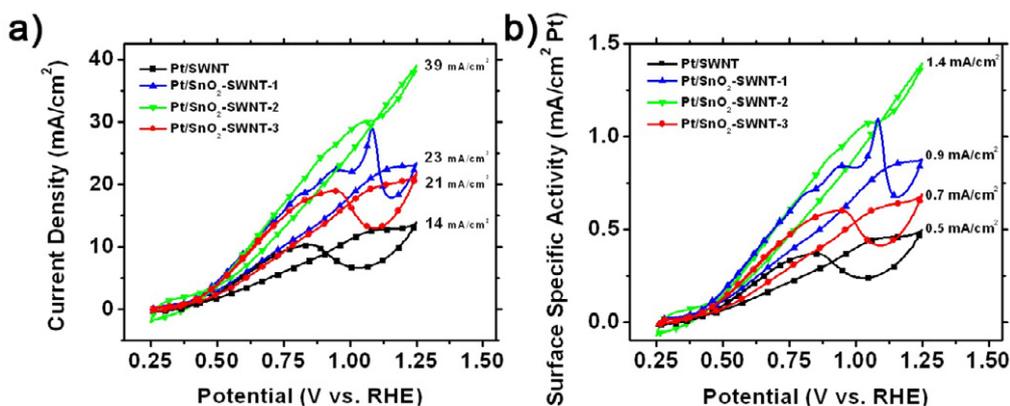


Figure 6. Ethanol oxidation (a) current density versus potential, and (b) specific catalytic activity versus potential of Pt/SWNT, Pt/SnO₂-SWNT-1, Pt/SnO₂-SWNT-2 and Pt/SnO₂-SWNT-3.

Acknowledgments

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